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PROCESS FOR DEINKING IMPRINTED PAPER

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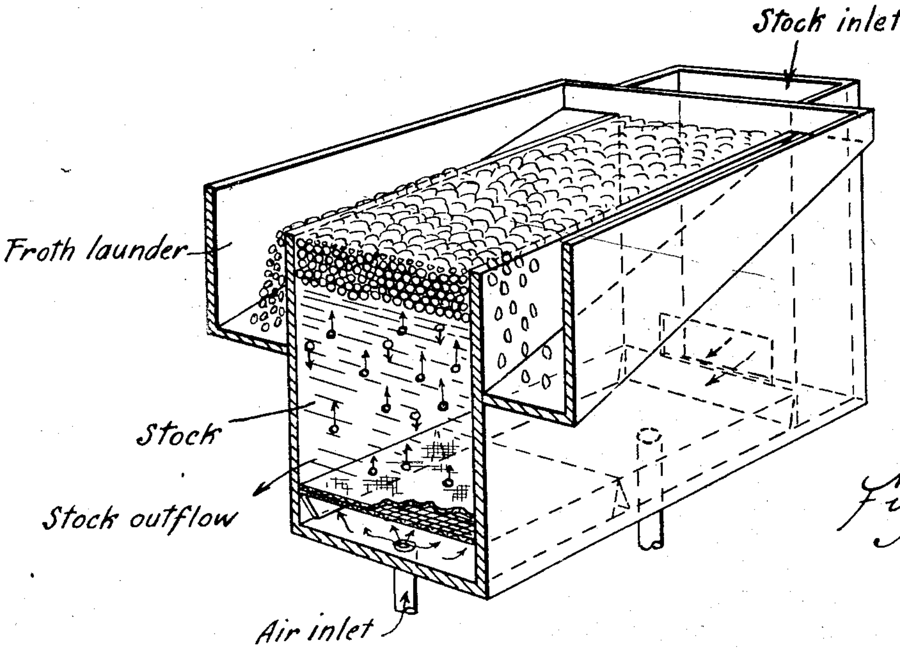

Fig. 1.

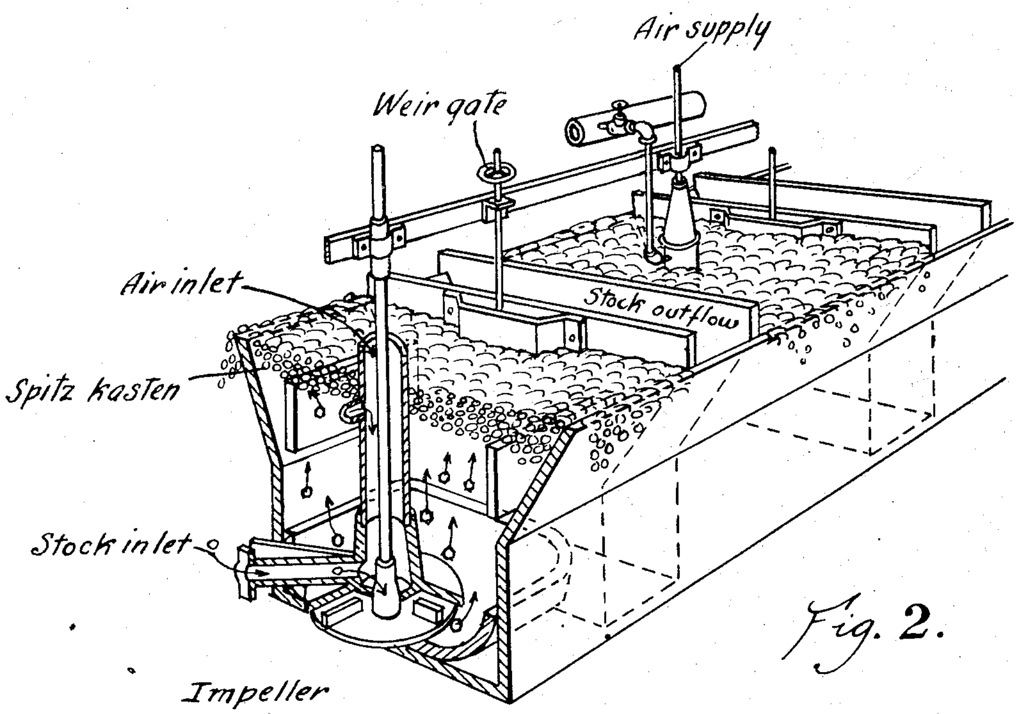

Fig. 2.

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PROCESS FOR DEINKING IMPRINTED PAPER

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Continuation of application Serial No. 625,209, July 27, 1932. This application May 25, 1934, Serial No. 727,577

11 Claims. (Cl. 92—9)

This application is filed in continuation and completion of my application filed July 27, 1932, Serial No. 625,209, allowed January 15, 1934.

The object of my invention is to provide an efficient and practical process for removing carbon inks from imprinted paper.

Waste imprinted paper may readily be reconverted into stock, but before such stock may again be used for making paper, the imprinted ink must be removed. In other words, the paper must be de-inked; for unless this is done the stock made from waste paper will have a dirty gray color, and is fit only for use in making low grade paper, or paper-board in which color is immaterial.

Various processes for de-inking imprinted paper have heretofore been used with more or less success. But these processes were not commercially practical, due either to excessive loss of paper stock and filler, or to the insufficient de-inking of the paper.

My invention has for its purpose to provide a process adaptable for de-inking papers of all classes—newspapers, magazines, ledgers and books—with a negligible loss of the paper stock and filler, and without deleterious effect upon the fiber composing the de-inked stock.

The carbon particles of the ink with which paper has been imprinted may be loosened from the paper fibers of imprinted paper and I have discovered that when the carbon particles have been freed from the fiber, they may then be removed by flotation in the form of a froth, so as to leave the fibers cleaned of the ink as a residuum.

By flotation I refer to a process similar to that employed for separating mineral; but before flotation can be accomplished the stock must be suitably prepared which preparation constitutes one of the essential steps of my invention.

I will now describe my invention by the various steps which it comprises.

Refining and cooking

Describing first the refining and cooking treatment of waste magazines, ledger and book papers, my process for de-inking imprinted paper is as follows:

By refining I mean the separation of the fibers from each other, (defiberizing) and producing stock suitable for making paper on a paper-machine.

The paper is first dusted, and preferably shredded. Shredding facilitates the reconverting of the paper into stock. The shredding operation may be conveniently performed in a hammer mill, or paper shredder available.

The shredded paper may be cooked, beaten, and refined by either one of two well-known methods; namely, by the circulating cooking-tank method, or the rotary-cooker method, but the cooking period may be reduced, with a view to economy in steam and time, to from 2 to 3 hours. For the complete removal of ink from the fiber is not essential in carrying out my de-inking process, since both carbon particles and ink-encrusted fibers are removed together from the stock by the subsequent de-inking steps. The stock may be cooked with some alkali, not exceeding the equivalent of 4% of caustic soda, for this may be used, for example caustic soda, soda ash, a mixture of lime and soda ash, or a mixture of lime, (calcium oxide,) and sodium silicate. The proportions of said chemicals are based on the dry weight of the paper stock. The consistency of the stock during the cooking step is generally 4–6%.

The cooking, beating, and refining effects the defiberization of the stock, and facilitates the separation of the carbon particles from the paper fibers and filler.

If newspaper only is to be defiberized and refined, the above-described process may be modified by proceeding as follows:

The newspapers are sorted, dusted and weighed, then preferably are shredded with one of the usual shredders in common use, and then is refined by thoroughly beating in a "broke" beater or beater commonly used in paper mills, or may be agitated in a tank by a pump, mechanical impellers, or similar means.

In the de-inking of newspapers, it is preferable that the temperature of the beater water be kept at from 140 to 160 degrees F. Newspaper defiberizes more easily in water of that temperature.

Approximately 25–30 lbs. of caustic soda, and four pounds of sodium silicate per ton of dry weight of newspapers are added to the beater. The paper is beaten or agitated for 45–60 minutes at a consistency of approximately 3%.

Consistency for flotation

The defiberized and refined stock from which the ink has been freed from the fiber must be brought to a proper consistency for flotation. The flotation operation is impeded by too thick stock and too thin a stock requires too much flotation cell capacity. A consistency of 1–1¼%, (80 to 100 parts of water to one of original paper by dry weight) is desirable.

Due to variations in sizing, certain waste papers require longer cooking and refining than others. In any event it is desirable to operate the flotation process continuously at a constant rate, and an agitated storage tank should be provided for the stock after it has been brought to a proper consistency, so that the flow of stock to the flotation apparatus may be maintained at a steady volume.

Flocculation of ink and dispersion of filler

The higher grade papers such as magazines, ledgers, and books are heavily sized with rosin, emulsified waxes and similar materials. The inks are incorporated with linseed oil and dryers, and the ink is dried by oxidation. When sized papers are cooked with an alkali, the size and oils are saponified. I have found that the carbon ink particles freed by the refining and cooking are dispersed due to the soaps present in the cooking liquor. The dispersion of the ink particles retards and hinders their removal by flotation, and therefore they should be flocculated, prior to flotation.

I have further discovered that the carbon ink particles may be flocculated, if the pH value is above 7.0, by adding burnt lime (calcium oxide), magnesium oxide or similar reagent. The lime and similar salts precipitate the sodium soaps which causes the ink particles to flocculate. Approximately 20 pounds of burnt lime per ton of original or dry weight of paper is sufficient for average No. 1 books and old magazines.

The dispersion of the mineral fillers in the paper retards their tendency to float off in the froth. I have found either sodium silicate or starch suitable dispersing agents when the pH value of the stock is above 7.0. Sodium silicate may be added at the rate of 10 lb. or less per ton of original dry weight of paper. If soluble starch is used, it may be used in amounts not exceeding 8 lb. per ton of dry paper.

Either lime or sodium silicate may be substituted for an equivalent amount of other alkali to assist in the cooking and refining operation.

If the stock has a pH value of less than 7.0 the addition of 4–10 lb. per ton of dry paper, of an acid, such as sulphuric, or one of the alum salts may be used to flocculate the ink and disperse the filler.

Effecting frothing and collecting by a suitable agent

I have discovered that the volume of froth from paper stock increases with the pH value from 7.0 upwards. If the pH value is below 7.0 it is necessary to use a large amount of frothing reagent of the heavier type as hereinafter specified.

The soaps formed in refining and cooking with an alkali of sized papers, also contribute to froth formation, since a small amount of size, from a paper-maker's standpoint, forms a relatively large amount of frothing agent, from a flotation standpoint. Rosins and similar soaps have strong frothing properties.

The presence of filler also assists in froth formation due to some filler always floating which encases or "armors" the froth bubbles, thus making a more persistent froth.

When stocks from magazines, ledgers, and books, according to my method have been cooked and refined by an alkaline process, the type and volume of flotation froth resulting, requires modification and correction. I have found the volume of froth may be reduced by lowering the pH value by a reagent such as sulphuric acid; also by the removal of the cooking liquor thus lowering the pH value as well as reducing the amount of saponified products present. The removal of cooking liquor may be accomplished by filtering or similar means immediately following the cooking and refining step. The volume of froth may also be reduced by the addition of 4–8 lb. of kerosene or similar reagent per ton of dry weight of paper treated, and this is probably the most practical method. It is usually desirable to modify the type of froth by the addition of one to two pounds per ton of dry paper, of a light frothing reagent, such as cresylic acid, pine oil, or one of the high boiling point synthetic alcohols, known commercially as "Du Pont Frothers."

Newsprint contains little or no size, and rarely fillers. The carbon inks are incorporated with mineral and fish oils and are dried by absorption. Newsprint is made with a large proportion of ground wood pulp which contains tannic acid. Tannic acid is toxic and prohibits froth formation. Hence it is difficult to obtain a sufficiently vigorous froth by a normal amount of frothing agent. I have found a suitable froth may be obtained by raising the pH value of the stock to 8.5–9.0 in combination with frothing reagents. The lighter frothing reagents may be used in amounts of approximately four pounds per ton of dry weight of paper. The heavier frothing reagents such as Barrets No. 4 coal tar oil, pine tar oil, hardwood creosotes may also be used, and it will be found advantageous to add these during the cooking and refining stage, thus to thoroughly incorporate them in the stock. The "Du Pont Frothers" are particularly good for newsprint.

It will be seen from the above that there are two extremes; highly sized and coated papers producing voluminous flotation froths, and newsprint giving insufficient flotation froths when the stock is cooked and refined by alkaline processes. The above discoveries will enable those skilled in the art of flotation not only to handle the above classes, but to intelligently treat intermediate and special classes of old papers, to be de-inked by my method.

If the paper stock to be de-inked has a pH value of below 7.0, flotation reagents both light and heavy, and in combination, may be used at the rate of 8 lb. and upwards per ton of dry paper.

The froth bubbles should be polygonal in shape with enough toughness to carry over well, and breaking down to liquid readily. The volume of froth should be less than 20% of the total volume of stock being floated, and a smaller volume is better. A thin or weak froth must be augmented as above mentioned for producing efficient separation and removal of the ink particles. Tough and persistent froths heavily encased or "armored" with filler, or roe-like froths should be modified by any of the means above described.

The ink particles are more readily removed by flotation if first flocculated and a reagent employed which has collecting properties for ink particles.

Some of the suitable collectors for ink have other properties such as detergent, frothing or froth-modifying properties. It is necessary that all the properties of any of the flotation reagents employed be thoroughly known not only in respect to carbon ink particles but also their action upon other paper constituents so that the fiber and filler are not floated off in the froth and no separation attained. This is most conveniently ascertained by trial and test in a laboratory flotation machine.

The high boiling point synthetic alcohols (commercially known as Du Pont Frothers) mentioned above under frothing reagents, also have excellent collecting properties for carbon ink particles.

Kerosene or similar products have excellent collecting properties, as well as being useful in modifying excessive froths, and it works well in connection with the Du Pont Frothers.

Sodium oleate if used in small amounts is an excellent collector of ink, but if used in large amounts disperses the carbon ink particles. If newsprint is to be de-inked sodium oleate may be added to the cooking step in the amount of two pounds or less per ton of dry paper. It has good detergent properties, as well.

Equal parts of amyl acetate and butyl alcohol have good collecting properties for carbon ink particles, and are excellent modifiers of heavy and voluminous froths. Two pounds or less of each per ton of dry paper should be used.

If the paper stock being floated has a pH value of below 7.0, potassium ethyl xanthate dissolved in ethyl chlor carbonate (commercially known as Minerec) is a good collector.

Since only a relatively small amount of some reagent is to be thoroughly incorporated in a very large amount of paper stock of the consistency required, the stock should be agitated for two to three minutes prior to flotation. This is termed "conditioning" in flotation work, and the stock from the storage chest may be pumped continuously to an agitating chest or tank of sufficient size to give proper "conditioning" time. If the stock requires the addition of water to dilute it to a proper consistency for flotation, the stock and water may be delivered continuously at constant rate to the conditioning tank, and the reagents added continuously at a constant rate at the same time by means of flotation reagent feeders.

It will be appreciated by those skilled in the art of flotation that the reagents may be added at other convenient points to take advantage of other properties or to give longer conditioning time, or to intensify the flotation operation at some later stage in flotation.

Removal of ink particles by flotation operation

The pulp is then delivered from the agitating tank to a flotation machine, similar to the machine now employed in mineral industry. Two examples of the common types of flotation machine I have shown in the accompanying drawing. These machines, showing diagrammatically in Fig. 1 a Callow pneumatic flotation cell; and in Fig. 2 showing a Fahrenwald subaeration mechanical cell, are so well known to the art that a detailed description of them is unnecessary.

Assuming that a multiple compartment or cell subaeration flotation machine is used and that the stock is introduced first in the third compartment, the first froth produced will be found heavier in ink than the froth from the succeeding compartments of the flotation machine.

The froth produced in the machine raises freed ink clots, and inky fibers from the stock, also some clean fiber and filler are entrained in the froth. The stock passes thru the remaining compartments of the flotation machine, and finally is discharged as a de-inked stock but with most of the mineral filler still in it.

The froth from the third and successive compartments of the flotation machine is returned to the first compartment and flows through the second compartment to the third, where it joins the original or primary feed into the machine making a closed circuit. This refloating of the froth produces a very inky froth, which is rejected and wasted. It also saves clean fiber and filler which have become entrained in the froth by returning the latter to the circuit. In this way the fiber and filler loss is confined substantially to very dirty fibers and filler material which have ink clots adhering to them, which I found to be about 2% to 5% of the original dry weight of paper.

In short, my flotation method may consist of two steps. The first step called "roughing," uses a dense, heavy collecting froth; the last compartments, in this case, acting as safety traps catching the occasional inky fiber and carbon particles which may have escaped; at the same time some clean fiber. The second step is the retreatment of the first froth termed "cleaning". The second froth is rich in inky fibers and carbon particles, and low in entrained clean fiber and filler, as a lesser number of fiber and particles are dealt with. The stock remaining after the second frothing or cleaning operation is then in about the same degree of cleanness as the original feed, and flows from the second compartment into the third, joining the original feed. This closed circuit enables the particles, or fibers if they have gone in the wrong direction to stay in the closed circuit until they are finally rejected.

In case a straight pneumatic flotation cell is used, the froth from the "rougher" cell is sent to a smaller "cleaner" cell, and the froth from the latter is rejected, and the stock from the "cleaner" cell is returned to the feed of the first or "rougher" cell.

The selection of the proper size of flotation machine should be made so as to give a frothing time in the first treatment of at least six to eight minutes. The specific gravity of the stock may, for practical purposes, be taken as 1. Paper stock stays in suspension for long periods compared to ore pulps and the vigorous action required in the mineral industry to keep the heavy minerals in suspension is not required in deinking paper.

The first froth generally breaks down readily into a stock of approximately the same consistency as the original stock treated by flotation. Spray water may be used to assist in breaking down the rougher cell froth before re-treatment in the cleaner cell with beneficial effects as lower consistencies assist the cleaner cell action appreciably.

In flotation work sometimes a third cleaning is done, and there are a number of combinations of "cleaner and rougher cells" used in flotation work as will suggest itself to anyone skilled in the art of flotation.

Removal of flotation reagents

The de-inked stock may then be filtered upon one of the well-known types of filters to remove flotation reagents and lightly washed, prior to bleaching or subsequent operations commonly employed for converting the stock into paper. The filtrate may be used for diluting the cooked and refined stock coming to the chest prior to flotation, thus saving water in bringing the stock to the required density. This filtrate carries the soluble reagents left in the stock and the amount of new reagents required is only that necessary to bring up the stock to the original amounts specified. This also saves very fine filler in the filtrate or white water which may have escaped the filtering or de-watering operation. The experienced operator will be able to judge from conditions in the flotation machine, and the characteristics of the froth, the necessary changes in amount of reagents when using returned filtrate water.

While it is desirable that a high percentage of the ink be freed from the fibers, it is not an essential to my method that the cooking be carried to the point where all the ink is absolutely freed and separated from the fiber, as the froth will pick up, and remove ink encrusted fibers as well as the carbon ink particles.

The rejected froth and inky fibers may be washed and used for board or other stock where whiteness is of no importance.

A laboratory flotation machine furnishes results which are dependable for controlling full scale results and may be used to determine in advance the best practice for operating under local or special conditions.

Illustrations of practical operation of my de-inking method

In de-inking old No. 1 magazines, the magazines are sorted for elimination of foreign matter and undesirable stock. The sorted magazines are shredded and sent to a broke beater; the broke beater discharging to a cooker of the circulating type.

The circulating type cooker, as usually employed is open to the atmosphere, and the stock is rapidly circulated by a large stock pump exterior to the tank; the heating is accomplished by live steam. The cooking is generally in batches.

A 6% consistency stock is furnished to the cooker together with 4% of caustic soda and 1% of burnt lime (calcium oxide). The temperature is brought up with steam to 190–210 degrees F. and the stock rapidly circulated for 3–4 hr. determined by test or sample to see the stock is thoroughly defiberized.

The cook is then discharged to a storage chest from which it is pumped at a constant rate by a stock pump to a conditioning chest. Water or filtrate from the finished stock is added at a constant rate to maintain the consistency in the conditioner at 1¼%. Reagents are then added at a constant rate by means of reagent feeders in the following amounts per ton of dry paper: eight pounds of kerosene, one pound of B–24 Du Pont Frother and two pounds of soluble starch. The conditioning tank should be of such size as to give three minutes conditioning time prior to flotation. The conditioned stock is preferably pumped by a stock pump so that a constant rate of feed to the flotation may be maintained.

The conditioned stock is sent to a "rougher" type of pneumatic flotation cell of such size as to give six minutes flotation time.

The first or rougher froth is sent by means of a launder to a cleaner cell of the pneumatic type, and the froth is well sprayed with wash water to break down the froth. The cleaner cell froth is roughly deckered, and the inky material wasted. Any coarse fiber caught by the decker due to operating errors may then be returned for re-treatment.

The cleaned stock from the rougher cell is sent to a filter, and the filtered stock is then sent for a lightbleach to the bleachery.

The stock from the cleaner cell may be sufficiently bright to be mixed with the clean stock from the rougher cell. If not, it is returned to the first or rougher cell for re-treatment.

The filtrate or white water from the filter is delivered to a storage tank, and may be used to dilute cooked stock in the conditioning tank, and for froth sprays, excess being wasted.

The following is an illustration of the application of my method for de-inking old newspapers.

The newspapers are sorted roughly for elimination of foreign matter and any undesirable waste paper.

The sorted newspapers are then shredded preferably in a wet type hammer mill, using water to carry the paper through the hammer mill, and into a circulating tank cooker.

The newspapers are cooked at a consistensy of about 3% with 25 lb. of caustic soda, and four pounds of sodium silicate per ton of dry newspaper. The temperature is maintained at 140 deg. F. and the cook rapidly circulated for one hour.

The defiberized stock is discharged to a storage chest, and from there pumped at constant rate to a conditioning tank. The stock is diluted to a consistency of 1¼% in the conditioning tank. Sufficient caustic soda is added to give a pH value of 9.0. to the 1¼% consistency stock. Four pounds of the Du Pont Frothers is added per ton of newsprint. The conditioner tank is of such size as to give three minutes agitation prior to entering the flotation circuit.

The conditioned stock is then fed to a pneumatic cell of sufficient size to give 6 minutes flotation time, the first or "rougher" froth going to a "cleaner" cell, the second or cleaner cell froth going direct to sewer or waste. The stock from the cleaner cell is returned to the head of the rougher cell for re-treatment.

The clean stock from the rougher cell is sent to a paper-mill decker and de-watered. The de-watered clean stock is then sent to storage chests. If any of the newspapers are brown from ageing, zinc hydrous sulphite may be used to brighten the stock, otherwise it is ready for paper.

The white water from the deckers is sent to a storage tank for use in diluting cooked stock in the conditioning tank, for spray water, and any excess is wasted.

I claim:

1. The process of de-inking paper which comprises refining and cooking the stock, with a chemical adapted to free substantially the ink particles from the pulp fiber, until tests show the stock to be defiberized and the fiber substantially freed from ink particles, effecting flocculation of the ink particles, and dispersion of other constituents by an agency selected relatively to the pH value of the stock, effecting frothing and collecting by a suitable agent, and removing the ink particles by froth flotation method.

2. The process of de-inking paper which comprises refining and cooking the stock, with a chemical adapted to free substantially the ink particles from the pulp fiber, until tests show the stock to be defiberized and the fiber substantially freed from ink particles, bringing the stock to a suitable consistency, effecting flocculation of the ink particles, and dispersion of other constituents by an agency selected relatively to the pH value of the stock, effecting frothing and collecting by a suitable agent, and removing the ink particles by froth flotation method.

3. The process of de-inking paper which comprises refining and cooking the stock, with a

chemical adapted to free substantially the ink particles from the pulp fiber, until tests show the stock to be defiberized and the fiber substantially freed from ink particles, bringing the stock to a consistency of approximately 80 to 100 parts of water to one part per dry weight of paper treated, effecting flocculation of the ink particles, and dispersion of other constituents by an agency selected relatively to the pH value of the stock, effecting frothing and collecting by a suitable agent, and removing the ink particles by froth flotation method.

4. The process of de-inking paper which comprises refining and cooking the stock, with a chemical adapted to free substantially the ink particles from the pulp fiber, until tests show the stock to be defiberized and the fiber substantially freed from ink particles, bringing the stock to a suitable consistency, effecting flocculation of the ink particles, and dispersion of other constituents by an agency selected relatively to the pH value of the stock, effecting frothing and collecting by a suitable agent, and removing the ink particles by froth flotation method including roughing and cleaning stages.

5. The process of de-inking paper which comprises refining and cooking the stock, with a chemical adapted to free substantially the ink particles from the pulp fiber, until tests show the stock to be defiberized and the fiber substantially freed from ink particles, bringing the stock to a suitable consistency, effecting flocculation of the ink particles, and dispersion of other constituents by an agency selected relatively to the pH value of the stock, effecting frothing and collecting by a suitable agent, removing the ink particles by flotation operation, and removing flotation reagents from cleaned stock.

6. The process of de-inking imprinted paper which comprises macerating the imprinted stock, adding, while agitating the stock, agents having alkaline, dispersing and collecting properties, cooking the paper stock until tests taken from the stock show the fiber to be substantially freed from ink particles, agitating the paper stock with a collecting agent, and a gelatinous material, reducing the paper stock with water to a low density, adding a frothing agent, the relative amounts of paper stock and agents above named being determined as hereinbefore described, producing frothing to effect flotation and thus the final separation of the inky froth from the paper stock, and removing the froth produced.

7. The process of de-inking imprinted paper containing ground wood and/or heavy filler which comprises refining and partially defiberizing the stock with a mild cook, reducing the stock with water to a low density, adding, while agitating, agents having dispersing and collecting and frothing properties, producing froth flotation and thus the partial separation of inky froth from the paper stock and removing the froth produced, screening out of the filler and fine fiber from the stock, subjecting the paper to a further strong cook until tests taken from the stock show the fiber to be substantially freed from inky particles, again reducing the stock with water to a low density, adding, while agitating, further agents having dispersing and collecting properties, the relative amounts of paper stock and agents above named being determined as hereinbefore described; and producing a frothing in the presence of a frothing agent, thus to effect the final separation of inky froth from the paper stock, and removing the froth produced.

8. The process of de-inking imprinted paper which consists in defiberizing the stock, adding agents having detergent and collecting properties, cooking the paper stock until tests taken show the stock defiberized and the fiber substantially freed from ink particles, reducing the stock with water to low density, the relative amounts of stock and agents above named being determined as hereinbefore described, producing frothing in the presence of a frothing agent, whereby to effect flotation and thus the final separation of the inky froth from the paper stock and removing the froth produced.

9. The process of de-inking imprinted paper which consists in defiberizing the stock, adding agents having detergent dispersing and collecting properties, cooking the paper stock until tests taken show the stock defiberized and the fiber substantially freed from ink particles, reducing the stock with water to low density, the relative amounts of stock and agents above named being determined as hereinbefore described, producing frothing in the presence of a frothing agent, whereby to effect flotation and thus the final separation of the inky froth from the paper stock and removing the froth produced.

10. The process of de-inking imprinted paper which consists in defiberizing the stock, adding agents having detergent and collecting properties, cooking the paper stock until tests taken show the stock defiberized and the fiber substantially freed from ink particles, reducing the stock with water to low density, the relative amounts of stock and agents above named being determined as hereinbefore described, producing frothing in the presence of a frothing agent, whereby to effect flotation and thus the final separation of the inky froth from the paper stock, controlling excessive frothing by a modifying agent, and removing the froth produced.

11. The process described by claim 8 including regulating the pH value by a suitable agency.

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